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Search for optimum conditions of Paulownia autohydrolysis process and influence in pulping process

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ABSTRACT

In this study we evaluated the potential of a species trihybrid fortunei Paulownia, tomentosa and elongata as an industrial crop in terms of its contents in holocellulose, lignin, xylo-oligomers, monomers and other glucan and its aprovecahamiento for making cellulose pulp. Well optimized biomass autohydrolysis processes yield valuable liquid and solid phases that can be used to produce liquid fuels and cellulosic pulp. This study focused on the optimization of autohydrolysis temperature and time during processing of *Paulownia fortunei x Tormentose x Elongate* hybrid wood.. The process was modelled in order to optimize the extraction of xylo-oligomers and xylose in the liquid phase while preserving the integrity of cellulose fibres. The optimum processing conditions (*viz.* temperatures of 180–195 °C and operating times of 0–15 min) provided an acceptable solid phase yield (70%), while maintaining a high xylose and xylo-oligomer contents in the liquid phase. Soda – anthraquinone pulping of solid fraction provide 60.6 % pulp yield at kappa number 33 and a viscosity of 787 cm^3/g. The autohydrolysed chips required 16.6 % less alkali than the regular chips to achieve kappa number 33.

Keywords: Autohydrolysis, biorefinery, paulownia, soda-AQ pulp, saccharides.

INTRODUCTION

The current European social development concerning the use of natural resources is not sustainable since it is largely based on fossil fuels, which are non-renewable and release large quantiteis of CO_2 to the atmosphere. There is a shortage of renewable raw materials in the market to attend the energy, pulp & paper and chemical industry sectors. The way to a sustainable development and resource renewability includes the searching/use of new resources and chemical and consumption products with which the lignocellulose forest biomass, and specially that one of high production of biomass capacity (energetic crops), shows as a "necessary" source of raw material due to its ubiquity, availability and "low pollutant character" [1, 2]. Biomass components fractionation would also allow the disposal of a variety of chemical products, for which technological development requires the integration of all stages, from farming and harvesting to the stages of fractioning and conversion to different products [3].

Paulownia crops present very high productions of biomass and re-sprouting capacity (more than 50 tons/ha/year, specially in annual crops, which are among the highest growing levels described in the literature [4].

Paulownia is one of these crops with very high productions of biomass and re-sprout capacity (more than 50 tons/ha/year, specially in annual crops, which are among the highest growing levels described in the bibliography [5]. Paulownia is a specie used for reforestation in China, where it is well known for more than 2600 years, but has naturalized since its introduction in United States and others parts of the world [6 - 8]. The genus Paulownia contains nine species. Most species of Paulownia are extremely fast growing, and can be harvested in 15 years for valuable timber [9]. It could be considered as a low demand water plant, in spite of not growing in barren zones [10, 11]. According to these authors the fiber length is around 0.84 mm for *Paulownia fortunei*, 0.94 for *Paulownia tormentosa* and average 1.12 for others 7 Paulownia species, similar to those found for Eucalyptus wood, whose typical values are 0.7-1.3 mm.

Suggested uses for Paulownia included veneer or plywood, furniture, handicrafts, tools, musical instruments, particleboard, charcoal and there also various attempts to generate energy from paulownia chips [9, 12 - 14]. One of them is its use as source for pulp. The most suitable variety of Paulownia for this purpose is *Paulownia Fortunei* [15], characterized by a fast development and an uniform and regular growth [12].

Another matter is the fact that in order to make integral use of vegetable species, its fractionation is necessary, but capable of providing a wide range of products in a similar way oil refineries do, following a scheme that could be summarised in the following sentence: "The biorefinery of tree: from pulp and paper to chemical products and energy" [2]. Currently, the identification of the best lignocellulose fractionation stages constitutes one of the most interesting fields for research and scientific development efforts [16] in a general framework of evaluation of the best lignocellulosic materials for their conversion and the contrast between biochemical and thermochemical platforms of conversion [17,18].The hydrothermal or autohydrolysis treatments is one of these possiblities. Using high temperature water, hydrolysis of acetyl group to acetic acid occurs. This acid acts as a catalyst, which produces the total or partial solubilization of hemicellulose. The acid treatment may be done in two stages, one of hemicellulose pre-hydrolysis and another of cellulose hydrolysis. Also interesting is the combination of autohydrolysis treatments with oxidation ones that dissolves/degrades lignin, leaving cellulose in solid state. Furthermore, the use of organic solvents to perform delignification has also been evalauted [19].

The hemicellulosic fraction of lignocellulosic biomass is made up of amorphous heteropolysaccharides containing xylose, arabinose, mannose, galactose and others. Xylan is the main hemicellulose component in hardwoods (including Paulownia) and many agricultural crops. The autohydrolysis process helps obtain a rich mixture in oligomers and some monomers. These compounds could be used as a commercial source of organic reagents [20]. In addition, the autohydrolysis process remove the extractives compounds which are presented in raw material [21]. Xylo-oligomers, from autohydrolysis of xylan, have food and pharmaceutical applications [22]. As food additives, xylo-oligomers have prebiotic properties derived from their preferential utilization by Bifidobacteria [23].

The solid fraction from the authohydrolysis process, characterized by its high content of lignin, hemicelullose and cellulose, could be employed as raw material for alcohol production [24], and particularly, an interesting alternative is its use as raw material for pulp and papermaking [25].

This study investigated the influence of the temperature and time of autohydrolysis for treating *Paulownia fortunei x Tormentose x Elongate* hibrid wood aiming at obtaining a valuable liquid phase and a suitable solid phase for cellulosic pulp production.

MATERIALS AND METHODS

Raw material. Provision and characterization

A trihybrid variety of Paulownia (Elongata x Fortuneii x Tormentose) clone obtained by in vitro replication . The material was harvested after three years of growth in plantations used to exploit biomass crops in Extremadura (southwestern Spain). The material was supplied by the firm Vicidex Europa. Paulownia wood trimming samples were milled to pass an 5-mm screen, because no diffusional limitations were observed for this particle size in the preliminary studies. Samples were air-dried, homogenized in a single lot (to avoid differences in composition among aliquots) and stored.

Aliquots from the homogenized wood (without compounds extraibles) lot were subjected to moisture determination (drying at 105 ºC to constant weight), quantitative acid hydrolysis with 5 ml of 72% sulfuric acid for an hour (Tappi T-248-em-85), and quantitative posthydrolysis with 4% sulfuric acid (adding water until 148.67g) at 121 ºC and 2 atm during 60 min in order to ensure quantitative conversion of oligomers into monomers [26]. Before HPLC analysis, the solid residue from posthydrolysis process was recovered by filtration and considered as Klason lignin. The monosaccharides and acetic acid contained in hydrolysates were determined by HPLC in order to estimate (after corrections for stoichiometry and sugar descomposition) the contents of samples in cellulose (as glucan), hemicelluloses (xylan + araban), and acetyl groups. The moisture of wood was considered as water in the material balances. Chromatographic determination was performed using an Agilent 1100 HPLC equipped with an ion-exchange resin BioRad Aminex HPX-87H column under the following conditions: mobile phase, 0.005 mol·L^{-1} of sulphuric acid; flow rate, 0.6 mL·min^{-1}; and column temperature, 50 °C. The volume injected was 20 μL. The holocellulose was determined with method of Wise et al. [27].

Autohydrolysis process and oligosaccharides determination

Wood chips and water were mixed in the desired proportions and reacted in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers. The vessels were heated up to maximum temperatures in the range 160 to 200ºC with external electric heaters. Process temperature was automatically controlled via an internal cooling coil equipped with circuit-opening electrovalves, which was used to cool the reactor after the highest temperature and operating time were reached.

At the end of treatment, the solid residue was recovered by filtration and washed with distilled water for gravimetric yield determination. An aliquot of liquors was filtered through 0.45 μm membranes and used for direct HPLC determination of monosaccharides and acetic acid. A second aliquot of liquors (25 ml) was subjected to quantitative posthydrolysis (with 4% sulfuric acid at 121 ºC and 2 atm during 60 min) before HPLC analysis. Operation conditions in HPLC are described in previous section for raw material. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis measured the concentrations of oligomers and acetyl groups bound to oligosaccharides [28].

Experimental Design for the Autohydrolysis Conditions. Multiple Regresion Model

To be able to relate the dependent (yield and glucose, xilose, arabinose and acetyl groups contents) and independent (temperature and time of process) variables in autohydrolysis process with the minimum testing, it was used a 2n central composite factor experimental design that enabled construction of second-order polynomial in the independent variables and the identification of statistical significance in the dependent variables. Independent variables were normalized by using the following equation:

$$X_n = \frac{X - \overline{X}}{(X_{max} - X_{min})/2}$$

Where X is the absolute value of the independent variable concern $\overline{X}$ is the average value of the variable, and X_{max} and X_{min} are its maximum and minimum values, respectively. Three levels of temperature (165ºC, 180ºC and 195ºC) and time (0, 15 and 30 min) were used in the autohydrolysis experiments.. The liquid/solid ratio is 12/1 in all experiments.

The number of tests required was calculated as $N = 2^n + 2*n + n_c$; 2^n being the number of points constituting the factor design, $2*n$ that of axial points and nc that of central points. Under our conditions, $N = 10$.

The experimental results were fitted to the following second-order polynomial:

$$Y = a_o + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1}^{n} c_i X_{ni}^2 + \sum_{i=1;j=1}^{n} d_i X_{ni} X_{nj} \quad (i < j)$$

The independent variables used in the equations relating to both types of variables were those having a statistical significant coefficient (viz. those not exceeding a significance level of 0.05 in the student ´s-test and having a 95% confidence interval excluding zero).

Pulping procedure

Cellulose pulps were obtained in the same reactor used in the hydrothermal pre-treatment. The initial liquor to solid ratio was 10:1 (dry wt. basis), with 8-23% of soda and 0.1% of anthraquinone (dry wt. basis), and pulping temperature and time of 160 ºC and 90 minutes, respectively. The reactor was then closed and simultaneously heated and actuated to assure good mixing and uniform swelling of Paulownia chips. When the pulping time elapsed, the reactor was chilled to a temperature of 25ºC. Following cooking, the pulp was separated from the liquor and disintegrated, without breaking the fibers, during 3 min. Pulping yield, Kappa number and viscosity were determinated according Tappi standard procedures 257, 236 and 230, respectively).

RESULTS AND DISCUSSION

Raw material characteristics

The chemical characterization of *Paulownia Fortunei x Tormentosa x Elongata*, *Paulownia Fortunei*, *Paulownia Tormentosa* [9, 29, 30] and other woods are shown in Table 1 [31 – 34], where the *Eucalyptus Globulus* was used as reference.

The cellulose content is 6.0%-17.6% (expressed as glucan), lower than those found for *Eucalyptus globulus*, but higher (22.2%-14.9%) that those found for *Paulownia Fortunei*, whereas lignin content is 17.6%-28.2%, higher than Eucalyptus's one [10, 11, 33]. Nevertheless, Paulownia have an elevated biomass production during its growth phase [35], so in a year it can develop the equivalent to several years of others species, such as wheat straw, sunflower, sorghum, olive, others woods etc. [29]. Each *Paulownia Fortunei* tree could produce a cubic meter of wood at the age of 5-7 years; it may grow in intensive plantations with about 2000 trees by ha. Then, it can be calculated an annual production of 330 tons/ha, nevertheless a more preservative number could be 150 tons/ha [11].

These production figures can be increased by using hybrids of several varieties. Ayan et al. [8] found the Fortunei + Tomentosa clone to grow especially well (72.6 cm from seed to one-year plants). The paulownia hybrid used in this work was harvested after 3 years of growth and produced more than 50 tons of biomass per hectare per year [36]. Its content in acetyl groups was the highest among the raw materials in Table 1, which is suggestive of an increased amenability to autohydrolysis –in fact, the acetyl/xylan ratio was 25% higher than in eucalyptus wood.

The holocellulose content was similar to that of eucalyptus and lower than that of Paulownia fortunei [9, 11, 29]; these previously reported values, however, were determined with the method of Wise et al. [27] and ours as a combination of monomers and oligomers. Lignin values are slight higher and xylan, araban and acetyl groups values are similar than that found for the others materials.

Autohydrolysis process. Modelling and optimization

Several experiences from isothermal autohydrolysis were carried out in order to study the effect of the process on the xyloolygomer production and cellulose degradation. Based on previous experiences on *Paulownia Fortunei* and others lignocellulosic materials [21, 30, 37 - 39], the operations were carried out at temperatures and times of process indicated in the experimental design.

In Table 2 the variations with the temperature and time of the different analyzed compounds (glucose, xilose, arabinose, acetyl groups and xilooligomers) of the liquid phase and solid phase yield are shown. The results were modelled by using the above-described multiple regression methodology. The ensuing models are shown in Table 3.

The discussion that follows focuses on the following assumption: autohydrolysis of the *Paulownia fortunei + elongata + tomentosa* clone provides an industrially useful liquid phase by virtue of its contents in xylose, xylo-oligomers and various other compounds the optimum processing conditions for which are those minimizing cellulose degradation in order to facilitate its subsequent exploitation specifically, as cellulose fibre for pulp and paper production.

The liquid phase yields (100 % - solid phase yield) are between 7.3% and 34.0% and include: monomers, oligomers, extractives and non volatile solids.

The yield was found to bear a linear, quadratic and binary (time × temperature) relationship to the independent variables. Interestingly, the quadratic terms had negative sign, which suggests that values in the upper segments of the variation ranges of the variables have an opposite effect and reduce ─or fail to increase─ the contents in monomeric sugars and the associated oligosaccharides as a result of increased degradation of xylose and xylo-oligomers and the presence of an increased concentration of the body of "other" products in the liquid phase. This is consistent with the content in this complex fraction corresponding to the experimental point (+1,+1) in the design of Table 1. The $X_t X_T$ interaction terms had a positive sign for the solid fraction yield upon autohydrolysis (i.e. a negative sign for the sugar and xylooligomer yield), which, again, is consistent with the prevalence of degradation of the extracted products over increased extraction of compounds from the solid phase at high temperature and time values, and also with the multiplying effect of a combination of high values of both independent variables.

Xilose, xilo-oligomers and others compounds contents showed important variations, in the range of 0.49-4.47%, 0.61-9.30% and 5.1-26.2% respectively. The variation of the concentration of "other" compounds was highly correlated with that of the xylose and xylo-oligomer content. The strongest dependence (xylose) was the linear dependence between the temperature and time, which suggests a strong effect of temperature and a lesser one of time on autohydrolysis (the coefficient for Xt was 44% smaller than that for X_T). However, the statistical significance of the $X_t X_T$ term, and the relatively small value of X_t, further support the previous inference that using higher autohydrolysis temperatures and lower times helps preserving the integrity of the cellulose polymer with little adverse effect on the xylose and xylo-oligomer contents of the autohydrolysis liquid phase.

The glucose content of the autohydrolysis liquid phase was only significantly dependent on the X_t and $X_T X_T$ terms. This does not contradict the widespread assumption that cellulose is heavily hydrolysed above 200 °C [33, 40], which was not considered here. Should cellulose be degraded at the lower temperatures used in this work, the residence time at a given temperature would have been more influential than the processing temperature itself. In theory, the cellulose degradation rate should increase with increasing temperature [41]; however, no such effect occurred judging by the statistical significance of the $X_t X_T$ term. Also, the fact that the term $X_T X_T$ was negative suggests that the autohydrolysis process reduces the glucose content of the liquid phase (an unequivocal result of cellulose hydrolysis at high

temperatures). This effect must inevitably be associated to the hydrolysis time and interpreted in the light of the fact that the non-influence of the autohydrolysis temperature on the linear terms is only relative and the result of the variable processing time prevailing over the variable temperature [42]. This strongly supports the starting hypothesis: inasmuch as the cellulose polymer must be preserved intact for future use, an appropriate combination of high temperatures and short operating times for the autohydrolysis process can lead to optimal extraction of oligomers and hence to efficient preservation of the integrity of the cellulose polymer.

One may assume an increased autohydrolysis temperature and time to lead to an increased content in xylo-oligomers in the liquid phase; however, the xylo-oligomers would be simultaneously or subsequently hydrolysed to sugar monomers or degradation products by effect of the higher time and temperature values [43]. The prevalence of either effect would account for the relative significance of the statistically significant terms in the equation used to model to the xylo-oligomer content (Y_{Xlo}). The quadratic and interaction terms are the greatest contributors here, both with negative sign; this suggests the need to operate in the central segments of the variation ranges in order to maximize the extraction of xylo-oligomers. The linear term for temperature in the autohydrolysis process, X_T, suggests the need to use high temperatures; the effect, however, may be lessened by the influence of other terms and its precise impact cannot be established simply by applying the proposed model.

In order to determine the values of the independent variables in autohydrolysis giving the optimum values of dependent variables, the response surfaces for each dependent variable were plotted (Figs 1).

The response surface representing the variation of yield in the autohydrolysis solid phase (Fig. 1a) confirms some of the above-described effects. Overall, the terms representing the influence of the operating time suggest opposing effects; also, the variable time appears to be scarcely significant with a view to increasing the yield in soluble compounds of the liquid phase −and decreasing the yield in the solid phase. The temperature does have a significant effect; overall, using values in the upper segment of its variation range maximizes the contents in soluble compounds of the liquid phase (or, in other words, minimizes the yield in the autohydrolysis solid phase).

The response surface for the glucose content of the autohydrolysis liquid phase (Fig.1b) strongly supports the previous hypothesis. If one aims at avoiding cellulose degradation and directing the autohydrolysis

process to hemicellulose polymers, then, based on Fig. 1b, the autohydrolysis temperature should be in the upper segment of its variation range and the operating time in its lower segment. Obviously, an identical effect can be obtained in the lower segment of the temperature range, albeit at the expense of a considerably reduced xylose content in the liquid phase. The most important inference here is that the operating time has a very strong effect on the extent by which the glucose concentration is increased; this suggests rapid degradation of the cellulose polymer and, again, the need to use short operating times.

The response surfaces for the contents in xylose (Fig. 1c) and acetyl groups (Fig. 1e) are similar, consistent with the similarity between the equations used to model the two variables. The overall effect of the processing time is insubstantial at temperatures in the lower segment of their variation range, but quite marked at levels in the upper segment. The autohydrolysis temperature has a more marked effect and allows extraction of xylose and acetyl groups to be maximized by using high levels of this variable. The combined effect of time and temperature on the xylose yield must be harmonized with the need to avoid cellulose degradation —and lower contents in the polymer as a result; this further supports the need to use temperatures in the upper segment of their variation range and medium to low values of the operating time.

The response surfaces for the contents in arabinose (Fig. 1d) and xylo-oligomers (Fig. 1f) are also similar. The slope from the lower to the central segments of their variation ranges are both very high, which suggests that hemicellulose degradation occurs at a high rate initially and a more moderate one at medium to low operating temperatures and times. This supports the hypothesis that the hydrolysis of hemicelluloses to xylo-oligomers competes with decomposition of the products. Clearly, the latter effect becomes increasingly prevalent as the operating temperature and time are increased, and is especially marked at a normalized value of +1 for both variables, where the xylo-oligomer content of the autohydrolysis liquid phase is strongly reduced. This further confirms the need to use a high temperature in combination with a medium to low operating time. The arabinose content warrants similar comments as the xylo-oligomers content.

Based on the foregoing, we optimized the operating temperature and time for the autohydrolysis of the *Paulownia fortunei + tomentosa + elongata* hybrid by using the software JMP, which affords adjusting dependent variables via specific independent variables. Thus, it allows one to fix an independent variable and change the other in order to examine the variation of dependent variables on a graph. In optimizing

the process conditions, we set to ensure that the autohydrolysis solid phase would be suitable for obtaining cellulose pulp of appropriate yield, kappa number and viscosity for papermaking purposes. Also, a compromise between high enough xylose and xylo-oligomer contents on the one hand, and low glucose contents in the liquid phase on the other, should be achieved (at temperature of 187 °C and operating times of 15 min).

Such conditions resulted in acceptable yield (70%), a low content in glucose (only 0.97% of the amount present in the starting raw material was extracted) and a high content in xylose and xylo-oligomers in the liquid phase (2.37 and 9.1% of the respective contents in the raw material).

NaOH-antraquinone pulping process of Paulownia fortunei x tormentose x elongate

Paulownia can be considered as promising plantation grown pulp wood [15]. In this work, solid fraction from autohydrolysis and raw material were delignified by using a NaOH-antraquinone pulping process. Table 4 show operational conditions (% NaOH) and results. These graphs allow one to approach the operating conditions for the pulping process following autohydrolysis in such as way as to obtain cellulose pulp with properties similar to those of a reference sample.

As can be seen, the yield obtained by pulping the autohydrolysed material with the same NaOH concentration as the reference pulp (PwA) was 5.7% lower. This can be ascribed to the autohydrolysed material having a more open structure and facilitating partial dissolution of hemicelluloses as a result. In fact, this facilitated penetration of the reagent into the raw material and led to more efficient delignification [44, 45]. On the other hand, reducing the NaOH concentration by 5% resulted in a higher yield and a kappa number still 35.2% smaller than with the reference conditions. Further reducing the alkali load made it inadequate for efficient delignification even though the material structure was more accessible by the reagent than in the unhydrolysed material. This reflected in an increased kappa number.

An autohydrolysis pretreatment in combination with alkaline pulping (16.6 % NaOH) was found to provide a valorizable liquid phase containing xylose and xylo-oligomers, and also to reduce the chemical load (27.8%) with respect to the reference pulp, all with and the same kappa number (33) and a increase in the yield of 7.5 percents all points. These results are quite comparable to those for kraft pulp from

Paulownia fortunei obtained with alkali loads of 14–16% [15], which were produced in yields of 44.5–51.0% and kappa numbers from 23 to 25.

The viscosity was lower (25.7%) for the pulp sample derived from autohydrolysed material at kappa number 33 by effect of celluloses being partly degrated [41, 46, 47]; this result, however, should be taken with caution since the product was brown pulp containing a variable amount of residual lignin.

CONCLUSIONS

A valuable liquid phase could be obtained from autohydrolysis process of *Paulownia Fortunei x Tormentose x Elongate*. The optimum of *Paulownia Fortunei x Tormentose x Elongate* autohydrolysis processing conditions could be an intermediate time and high-intermediate temperature (*viz.* temperatures of 180–195 °C and operating times of 15 min). In these conditions, degradation of solid phase is minimal and a material high in cellulose content could be obtained, while the xylose recuperation is maximal in a liquid phase high in xylose and xylo-oligomers contents. The autohydrolysis treatment of paulownia chips decreased chemical demand in subsequent NaOH-anthraquinone pulping (25%), while pulp production gives a good yield and viscosity at a given kappa number when compared to the reference chips not autohydrolyzed.

ACKNOWLEDGEMENTS

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Table 1: Chemical composition of *Paulownia* and other pulp raw materials

Chemical Composition (percentages oven dry matter basis)	*Paulownia Fortunei*			*Paulownia Tormentosa*		*Eucalyptus Globulus*		Kenaf	Miscanthus	Aspen	Paulownia (fortunei x tormentosa x elongata)
	Caparros et al.[30]	Jimenez et al. [11]	Rai et al. [15]	Kalaycioglu et al. [9]	Olson and Carpenter [10]	Garrote et al. [33]	Ververis et al. [34]	De Vrije et al. [32]	Ververis et al. [34]	Ebringerová and Heinze [31]	Present study
Holocellulose	56.9	70.9	69.6	78.8	n.d.	66.9	n.d.	n.d.	n.d.	n.d.	65.2
Klasson lignin	27.2	22.4	28.0	22.1	20.9	22.9	n.d.	19.3	n.d.	19.3	27.8
Glucan	34.2	37.4	n.d.	48.3	40.7	46.8	53.4	36.3	39.5	36.3	44.0
Xylan	18.3	n.d.	n.d.	n.d.	n.d.	16.6	14.2	22.7	19	22.7	15.7
Araban	1.1	n.d.	n.d.	n.d.	n.d.	0.54	0.4	0.6	1.8	0.6	1.1
Acetyl groups	3.3	n.d.	n.d.	n.d.	n.d.	3.56	n.d.	n.d.	n.d.	n.d.	4.4

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Table 2: Values of Independent Variables and composition of the liquid fractions and solid yield obtained

in the autohydrolysis Process Using the Proposed Experimental Design.

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Normalized values of time (X_t), temperature (X_T)		Yield, %	Glucose, %[*]	Xylose, %[*]	Arabinose, %[*]	Acety Groups, %[*]	Xylo-oligomers, %[*]	Others, %[*]
0	0	74.0	1.00	1.37	0.59	0.13	9.27	13.70
0	0	74.5	0.99	1.45	0.56	0.10	9.30	12.00
1	1	66.0	0.98	4.47	0.26	0.31	1.82	26.00
1	-1	81.0	0.98	0.81	0.52	0.09	7.51	9.10
-1	1	70.3	0.87	2.59	0.39	0.17	8.81	16.90
-1	-1	92.7	0.88	0.49	0.13	0.06	0.61	5.10
1	0	71.7	1.02	2.39	0.54	0.17	8.16	16.10
-1	0	79.2	0.94	0.92	0.45	0.08	7.81	10.80
0	1	67.0	0.93	3.32	0.41	0.22	7.45	17.00
0	-1	84.2	0.93	0.57	0.40	0.07	5.93	9.30

* percentages oven dry matter basis

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Table 3: Equations yielded for each dependent variable.

No Eq.	Equation	r^2	F-Snedecor
1	$Y_{yie} = 74.066 - 3.916\,X_t - 9.092\,X_T + 1.591\,X_t\,X_t + 1.742\,X_T\,X_T + 1.850\,X_t\,X_T$	0.998	372
2	$Y_{glu} = 0.989 + 0.060\,X_t - 0.059\,X_T\,X_T$	0.973	130
3	$Y_{xy} = 1.532 + 0.614\,X_t + 1.417\,X_T + 0.509\,X_T\,X_T + 0.391\,X_t\,X_T$	0.990	135
4	$Y_{ar} = 0.572 + 0.059\,X_t - 0.079\,X_t\,X_t - 0.168\,X_T\,X_T - 0.13\,X_t\,X_T$	0.994	132
5	$Y_{ac} = 0.120 + 0.044\,X_t + 0.079\,X_T + 0.032\,X_T\,X_T + 0.024\,X_t\,X_T$	0.984	77
6	$Y_{xlo} = 9.482 + 0.671\,X_T - 1.702\,X_t\,X_t - 2.992\,X_T\,X_T - 3.471\,X_t\,X_T$	0.995	186

Where Y_{yie}, Solid fraction after autohydrolysis yield (%). Y_{glu}, Y_{xy}, Y_{ar}, Y_{ac}, Y_{xlo}, Glucose, xilose, arabinose, acetyl groups and xylo-oligomers contents in liquid phase respect initial raw material (dry basis), respectively. X_t, X_T, normalized autohydrolysis time and autohydrolysis temperature, respectively.
The differences between the experimental values and those estimated by using the previous equations never exceeded 5% of the former (10% for glucose and acetyl groups).

Figure 1: (a)Yield, (b) glucose, (c) xylose, (d) arabinose (e) acety groups, (f) xylooligomer, variations as a function of temperature and time of autohidrólisis process.
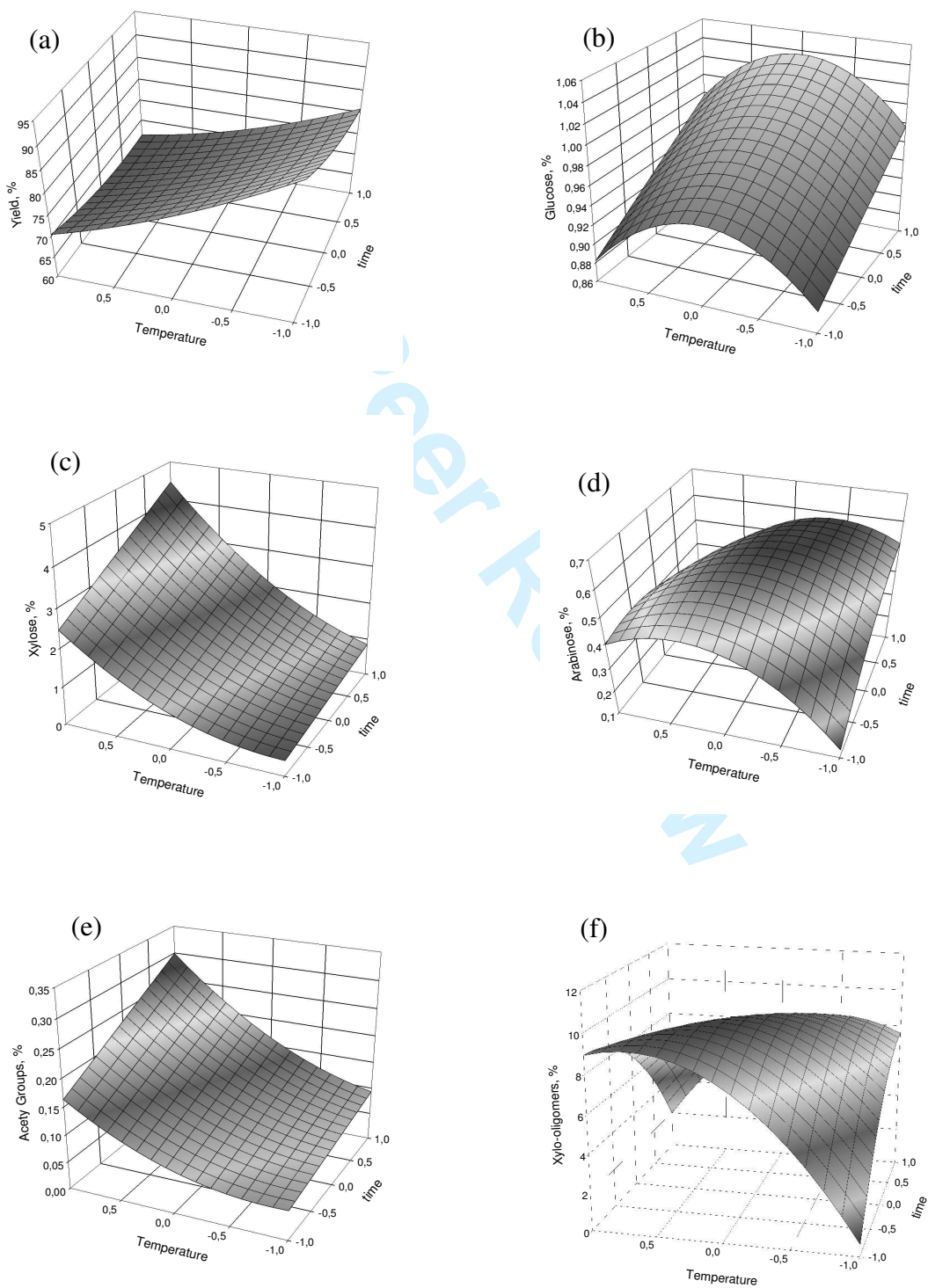
Table 4: Variation in yield (a), Kappa number (b) and viscosity (c) vs NaOH concentration, of pulps from *Paulownia Fortunei x Tormentose x Elongate.* NaOH- anthraquinone process. **PwA** Pulp without autohidrólisis; **PaA** Pulp after autohidrólisis.

Pulping Conditions	Yield, %	Kappa Number	Viscosity, cm^3/g
PWA	53,10	33,61	1059,90
PaA 23% Sosa	50,09	14,42	704,83
PaA 18% Sosa	57,29	21,78	748,17
PaA 13% Sosa	70,67	74,16	966,40
PaA 8% Sosa	88,22	160,3	1381,92